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Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh

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Abstract

Sediment from two deep boreholes (~400 m) approximately 90 km apart in southern Bangladesh was analyzed by X-ray absorption spectroscopy (XAS), total chemical analyses, chemical extractions, and electron probe microanalysis to establish the importance of authigenic pyrite as a sink for arsenic in the Bengal Basin. Authigenic framboidal and massive pyrite (median values 1500 and 3200 ppm As, respectively), is the principal arsenic residence in sediment from both boreholes. Although pyrite is dominant, ferric oxyhydroxides and secondary iron phases contain a large fraction of the sediment-bound arsenic between approximately 20 and 100 m, which is the depth range of wells containing the greatest amount of dissolved arsenic. The lack of pyrite in this interval is attributed to rapid sediment deposition and a low sulfur flux from riverine and atmospheric sources. The ability of deeper aquifers (>150 m) to produce ground water with low dissolved arsenic in southern Bangladesh reflects adequate sulfur supplies and sufficient time to redistribute the arsenic into pyrite during diagenesis.
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1. INTRODUCTION

Arsenic substitution into early diagenetic pyrite and acid-volatile sulfide (AVS) is commonly proposed as a mechanism to account for removal of dissolved arsenic from pore water in marine and fresh water sediment (Farmer and Lovell, 1986; Huerta-Diaz and Morse, 1992; Sullivan and Aller, 1996; Hideki and Yoshihisa, 1997; Saunders et al., 1997; Huerta-Diaz et al., 1998; Pirrie et al., 1999; Mucci et al., 2000; Sternbeck et al., 2000; O'Day et al., 2004; Saunders et al., 2005b; Southam and Saunders, 2005; Wilkin and Ford, 2006). Arsenic assimilation into forming sulfides commonly occurs as sediment is buried below the suboxic and sulfidic redox boundary. Masuda et al. (2005) observed arsenic-bearing oxides in shallow intertidal sediment off the coast of Japan and arsenic-bearing sulfides deeper in the sediment column. Sullivan and Aller (1996) report that arsenate in shallow Amazon shelf sediments is chemically reduced during burial, released to solution and removed from pore waters with increasing depth. Similarly, Moore et al. (1988) determined that arsenic bound to iron oxyhydroxides was redistributed into sulfide in reservoir sediment on the Clark Fork River, Montana.

The arsenic contamination in south and southeast Asia is attributed to redox changes, paleogeography, and tectonic setting whereby uplifted bedrock containing arsenic-rich minerals is weathered, rapidly eroded, and deposited in alluvial basins (Acharyya et al., 2000; Saunders et al., 2005a). The generally accepted model for high levels of dissolved arsenic proposes that arsenic released during weathering is absorbed onto neoformed ferric oxyhydroxides. During burial, bacteria use available organic matter to reductively dissolve the ferric oxyhydroxide grain coatings and release the arsenic to solution (Nickson et al., 2000;

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Berg et al., 2001; BGS and DPHE, 2001; Harvey et al., 2002; Islam et al., 2004; van Geen et al., 2004; Islam et al., 2005). Arsenic release by in situ oxidation of sulfide minerals in response to lowering water levels has been proposed but largely dismissed because of the lack of correlation of arsenic with dissolved sulfate (Acharyya, 2002). Independent of origin, the fate of dissolved arsenic in ground water is incompletely known. Arsenic-rich ground water either directly discharges into the Bay of Bengal or as base flow into rivers, which results in eventual flushing of labile arsenic from the aquifers. Alternatively, arsenic may be retained in the sediment in authigenic iron sulfide minerals. Both flushing and trapping of arsenic in sulfides would support the use of 'deeper' aquifers as a source of safer drinking water but risk evaluation would be markedly different depending on the relative importance of these two processes.

Although iron sulfide has been recognized as a constituent of the sediment in the Bengal Basin (Chatterjee et al., 1995; Nickson et al., 2000; BGS and DPHE, 2001; Acharyya, 2002; Stuben et al., 2003; Akai et al., 2004; McArthur et al., 2004; Swartz et al., 2004; Polizzotto et al., 2005; Ravenscroft et al., 2005), its relative importance and relation to the extensive arsenic-contaminated ground water in south and southeast Asia has not been fully evaluated. This study presents new information on the vertical variations in the abundance and morphology of iron sulfide, its arsenic content, sulfur isotope composition, and factors controlling its formation in shallow and deep sediment in southern Bangladesh.

1.1. Setting

The sediment underlying the villages of Rajoir and Srirampur in Bangladesh (Fig. 1) were selected to evaluate the ability of deeper (>150 m) aquifers to provide safe drinking water. The town of Rajoir (N 23.206; E 90.049), in the Rajoir upazila, Madaripur district, is 30 km south of the Padma River and 50 km west of the Meghna River. It is located on the lower Ganges floodplain and is typical of As-contaminated areas located on regularly flooded and actively aggrading floodplains. According to results presented by the National Arsenic Mitigation Information Center (NAMIC), approximately 71% of the 1340 wells tested within 3 km of the town of Rajoir exceed the Bangladesh drinking water standard of 50 μg/L; similar frequency of high dissolved arsenic is reported for the greater Rajoir upazila (75% of 13,000 wells) (www.bwspp.org/photo_albam.html#screening%20Resulat). Srirampur (N 23.339; E 90.922) is a village in Kachua upazila, Chandphur district, 30 km east of the Meghna River. It is located on the lower delta and is part of the extensive flood basin considered part of the Meghna Estuary. The Srirampur borehole was located on alluvium whose surface is above normal levels of flooding, but may be inundated during an unusually large flood. Wells near Srirampur typically contain >50 μg/L dissolved arsenic (99% of 3300 wells tested), which is similar to the 98% reported for the nearly 18,000 wells tested in the Kachua upazila (www.bwspp.org/photo_albam.html#screening%20Resulat). The high proportion of contaminated wells highlights the critical need for alternative supplies of drinking water in both areas.

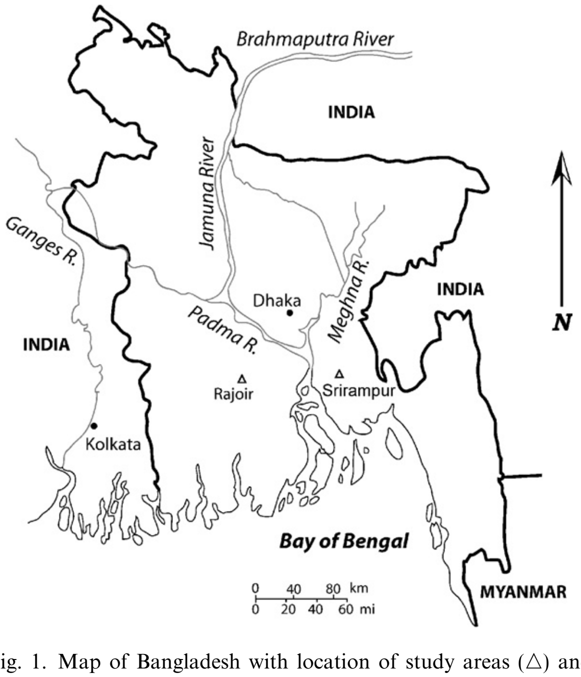

Fig. 1. Map of Bangladesh with location of study areas (△) and major cities (●).

As indicated by Ravenscroft et al. (2005), the stratigraphy of the Bengal Basin is poorly described. High Himalayan crystalline rocks have been the dominant source of sediment to the Bengal Basin since the Miocene. The thickness of sediment sampled for this study (450 m) is inferred to have been deposited mainly in the Quaternary, though Pliocene deposits may be present. The sediment sampled likely was deposited in a range of environments evident in the modern Bengal Basin. Fluvial channel, flood plain, estuarine, and deltaic deposits are stacked vertically and transition laterally. The complex spatial variability is attributed to changes in sea level, glaciation, tectonics and shifting river courses. Differences in the physical and chemical conditions of each of the depositional settings have been proposed to explain the kilometer-scale spatial heterogeneity of dissolved arsenic concentrations (van Geen et al., 2003, 2006; McArthur et al., 2004).

2. METHODS

2.1. Sampling

Sediment samples were collected from active sand bars in the Meghna and Padma rivers; from 4 hand-dug excavations <5 m deep; and from cored intervals of two boreholes drilled to depths up to 450 m during 2003 and 2004 at Rajoir and Srirampur (Fig. 1). Sand bars were sampled using local watercraft. Shallow excavations included in this study were sampled where encountered during fieldwork within 5 km of the borehole locations.

Procedures used during sediment collection and chemical analyses are summarized below and presented in greater detail in Breit et al. (2006, 2007). Selected depth intervals of